electronic reprint

Journal of
Applied Crystallography
ISSN 0021-8898

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J. Appl. Cryst. (1999). **32**, 536–542

Zeolite structure determination from powder diffraction data: applications of the *FOCUS* method

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(*Received 12 November 1998; accepted 2 March 1999*)

Abstract

The *FOCUS* approach to zeolite structure determination from powder diffraction data has been applied to data from four different zeolitic materials. The solutions of the structures of two aluminophosphate molecular sieves, YUL-89 (AWO topology) and YUL-90 (ZON topology), are used to demonstrate routine applications of the procedure. The high-silica zeolite ZSM-5 (MFI topology), which has 12 Si atoms (38 framework atoms) in the asymmetric unit, and the gallophosphate cloverite (-CLO topology), the framework of which is not fully fourfold connected, provide examples of extreme cases, which challenge the limits of the *FOCUS* algorithm. Taken together, the four examples give an overview of the practical aspects of the *FOCUS* method and illustrate its potential and its limitations.

1. Introduction

The determination of a zeolite structure from powder diffraction data is generally a non-trivial matter. These materials tend to crystallize with relatively high symmetries and large unit cells, and this automatically leads to a high degree of reflection overlap. With the resulting ambiguity in the relative intensities of the individual reflections, the application of conventional direct methods of structure solution, which rely upon the intensities being correct, often fails. Furthermore, in contrast to molecular materials, where the connectivity and certain aspects of the molecular geometry are usually known in advance, the connectivity of these extended framework structures is unknown.

It is known, however, that these open framework structures can all be described as three-dimensional four-connected nets of tetrahedrally coordinated atoms (T atoms), such as Si, bridged by O atoms. To circumvent the reflection-intensity ambiguity problem, while taking advantage of the crystal chemical information common to all zeolite framework structures, the program *FOCUS* (Grosse-Kunstleve *et al.*, 1997) was developed. *FOCUS* combines an automatic Fourier recycling algorithm with a specialized topology (framework) search specific to zeolites. The flowchart given in Fig. 1 shows the *FOCUS* program in the context of the complete structure determination procedure. The zeolite-specific crystal chemical information is used in the interpretation of the electron density maps generated in the Fourier recycling loop. Assignment of atom type to the peaks is based either on the peak height, cell contents and interpeak distance (atom recycling) or on the largest framework fragment found in the topology search (framework-fragment recycling). Any complete three-dimensional four-connected topology found is classified and stored in a file. The topology found most frequently is usually the

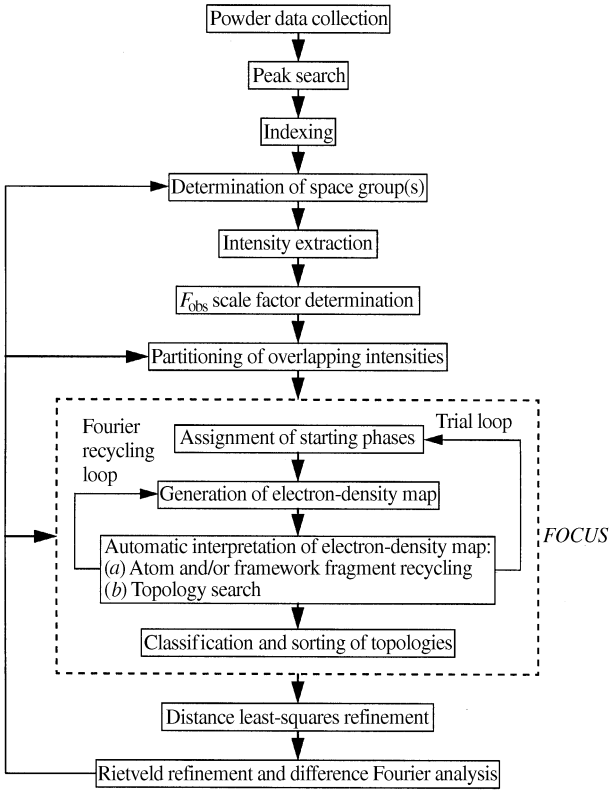

Fig. 1. The *FOCUS* environment.

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correct one. Further details of the *FOCUS* algorithm can be found in the paper cited above.

FOCUS was applied successfully to a number of molecular sieve structures, some test cases and some previously unknown structures, as it was developed (Grosse-Kunstleve, 1996; McCusker *et al.*, 1996). Recently, Kirchner *et al.* (1999), Wagner *et al.* (1999), Shantz *et al.* (1999) and Brenner *et al.* (1999) have also used *FOCUS* to solve the novel structures of AlPO-53(C), SSZ-44, MCM-61 and a new high-silica zeolite, respectively. In this paper, four further examples, which illustrate some of the practical aspects of this approach, are described.

The first two materials, the aluminophosphates YUL-86 and YUL-90, were synthesized in fluoride medium by Guth and co-workers (Guth, 1995), and were thought to have novel crystal structures. Although application of the *FOCUS* method quickly revealed that both phases had known framework topologies [YUL-86 has the $AlPO_4$-21 (AWO) topology (Parise & Day, 1985), and YUL-90 the ZAPO-M1 (ZON) topology (Marler *et al.*, 1995)], the results provide valuable examples of typical structure determinations with the *FOCUS* method.

The other two materials, the high-silica zeolite ZSM-5 (van Koningsveld *et al.*, 1987) and the gallophosphate cloverite (Estermann *et al.*, 1991), were chosen because they provide examples of extremely difficult cases. For ZSM-5, the number of topologically distinct tetrahedral framework sites (T sites) is 12, the largest number found in the *Atlas of Zeolite Structure Types* (Meier *et al.*, 1996). Cloverite was chosen because the refined structure has the largest unit cell of all structures referenced in the *Atlas of Zeolite Structure Types* (space group $Fm\bar{3}c$ with $a = 51.7$ Å), and because it has the additional complication that the framework is not fully four-connected. Of the five topologically distinct T sites in cloverite, one is only connected to three other T sites (*via* O atoms); the fourth bond is satisfied by an OH group.

Taken together, these four examples demonstrate both the potential and the limitations of the *FOCUS* method. To illustrate the working of the program, and to convey the ideas behind it, the input files are described in more detail than in the previous paper.

2. Data collection and intensity extraction

The aluminophosphate samples were kindly provided by Professor J.-L. Guth and the cloverite sample by Professor H. Kessler, both from the Université de Haute-Alsace in Mulhouse, France. The ZSM-5 sample was prepared in-house using a standard synthesis procedure. Data for the two aluminophosphates YUL-86 and YUL-90 were collected on 0.3 mm capillary samples mounted on a laboratory Stoe Stadi P diffractometer equipped with a linear position-sensitive detector (PSD) using strictly monochromatic Cu $K\alpha_1$ radiation. A second data set for the aluminophosphate YUL-86 was collected on the Swiss–Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, with the sample in a 1.0 mm capillary and a predetector Ge(111) analyzer crystal. Comparison of the results obtained with the two data sets for YUL-86 illustrates the importance of using high-resolution data.

Data for ZSM-5 were also collected on the SNBL instrument, but in Debye–Scherrer mode (*i.e.* a simple receiving slit instead of the analyzer crystal) with the sample in a 0.5 mm capillary. Data for cloverite were collected on beamline 8.3 at the Synchrotron Radiation Source (SRS) in Daresbury, UK, with a flat-plate sample and long predetector Soller slits (Cernik *et al.*, 1990). Details of the various data collection parameters are given in Table 1.

For the two aluminophosphates, initial lattice parameters were obtained by running the *PEAKFIND* program (Alexander, 1973), and using the peak positions as input for the *POWDER* (indexing) program of Taupin (1989). For all data sets, the background intensity was determined manually and then *GSAS* (Larson & von Dreele, 1995) was used to extract integrated intensities up to a resolution of 1.31 Å. The final values for the refined profile parameters (all *GSAS* parameters are defined in the *GSAS* user manual) are also given in Table 1.

3. Structure determination of the aluminophosphate YUL-86

3.1. *FOCUS input files*

The *FOCUS* input file for YUL-86 (Stoe measurement) is provided as an example in Fig. 2. A detailed description of all *FOCUS* keywords is available in a thesis by Grosse-Kunstleve (1996) or on the World Wide Web at http://www.kristall.ethz.ch/LFK/software/soft.html (including complete input files for all examples presented herein). In the following sections, only the most significant parts of the input files are highlighted.

For clarity, the file in Fig. 2 has been divided into blocks separated by empty lines. The first block is self-explanatory. The *AtomType* lines in the second block define the cell contents of the structure to be solved and tell the program which atom types are nodes and which are bridging atoms. In the next block, information for the Fourier recycling procedure based on the assignment of atoms to the highest peaks in the electron density map (atom recycling) is supplied. Most important are the individual minimum distances for each pair of atom types. It should be noted that, in contrast to the framework-fragment recycling mode, bonding is not considered in the atom recycling mode. The minimum distances apply to all pairs of atoms, whether they are bonded or not.

Table 1. *Summary of the data collection and intensity extraction parameters for all samples*

All *GSAS* parameters are defined in the *GSAS* user manual (Larson & von Dreele, 1995).

		YUL-86	YUL-90	ZSM-5	Cloverite
Chemical formula		$[Al_{12}P_{12}O_{48}]\cdot x$*R*F	$[Al_{32}P_{32}O_{128}]\cdot x$*R*F	$[Si_{96}O_{192}]\cdot$4TPAOH	$[Ga_{768}P_{768}O_{2976}(OH)_{192}]\cdot 192$*R*F
Data collection					
Instrument	Stoe STADP-I	SNBL	Stoe STADP-I	SNBL	SRS
Detector	Linear PSD	Ge(111) analyzer crystal	Linear PSD	No analyzer crystal	Long Soller slits
Sample	0.3 mm capillary	1 mm capillary	0.3 mm capillary	0.5 mm capillary	Flat plate
Radiation	Cu $K\alpha_1$	λ = 1.0529 Å	Cu $K\alpha_1$	λ = 1.1011 Å	λ = 1.7047 Å
2θ range (°)	8–70	3.1–49	8–70	5–60	3.5–80
Step size (° 2θ)	0.02	0.01	0.02	0.01	0.01
Intensity extraction					
Space group	$P2_1/c$	$P2_1/c$	*Pbca*	*Pnma*	$Pm\bar{3}m$
a (Å)	8.632	8.633	14.548	20.063	25.856
b (Å)	17.696	17.704	15.301	19.938	
c (Å)	10.377	10.381	16.629	13.409	
β (°)	123.68	123.66			
GU	106.5	29.9	144.2	16.3	15.5
GV	−48.5		−102.4	−0.1	−11.9
GW	24.0		27.9	3.1	3.2
LX	4.360	2.362	2.804	0.373	1.758
LY		0.099	3.674	5.097	14.165
Asym.	1.6197	0.5949	1.7591	0.3820	0.0082
R_p	0.0373	0.0588	0.0475	0.0371	0.0626
R_{wp}	0.0495	0.0879	0.0693	0.0529	0.1067

```
Title YUL-86 2.scan 0.3 cap STOE PSD  95-05-27 GSAS extraction

SpaceGroup  P 1 21/c 1
UnitCell    8.6327  17.6959  10.3772   90.000  123.676   90.000

AtomType  +  Node        Al  12
AtomType  +  Node        P   12
AtomType  -  NodeBridge  O   48

Chemistry  MinDistance  Node        Al    Node        Al    2.6
Chemistry  MinDistance  Node        Al    Node        P     2.6
Chemistry  MinDistance  Node        Al    NodeBridge  O     1.4
Chemistry  MinDistance  Node        P     Node        P     2.6
Chemistry  MinDistance  Node        P     NodeBridge  O     1.4
Chemistry  MinDistance  NodeBridge  O     NodeBridge  O     2.3
MaxPotentialAtoms  96
MaxRecycledAtoms   24

FwSearchMethod  FwTracking
MaxPeaksFwSearch  128
MaxPeaksFwFragmentSearch  64
MinNodeDistance  2.6
MaxNodeDistance  3.6
MinSymNodes  0
MaxSymNodes  32
NodeType  4  *  -6 -3 -1 4 6
MinLoopSize  4
EvenLoopSizesOnly  On
Check3DimConnectivity  On
IdealT_NodeDistance  3.1
CheckTetrahedralGeometry  Normal

RandomInitialization  Time
FeedBackCycles  1 1 1 1 1 1 1 1 1 1

Grid_xyz  26  54  32
eDensityCutOff  1 %
MinPfI  17
CatchDistance  0.5

Lambda  CuA1
FobsMin_d  1.40
FobsScale  0.09
OverlapFactor  .15
OverlapAction  EqualMF2
ReflectionUsage  75 %
```

Fig. 2. *FOCUS* input for YUL-86; Stoe measurement.

The block starting with *FwSearchMethod* (framework search method) specifies the parameters for the framework and framework-fragment search procedure. *MinNodeDistance* and *MaxNodeDistance* establish the lower and upper limits for bonded node–node distances. Usually a tolerance of 0.5 Å around the 'ideal' distance of 3.1 Å is allowed. *MinSymNodes* and *MaxSymNodes* set the lower and upper limits for the number of framework nodes per unit cell. Normally, the choice for *MaxSymNodes* is based on the consideration that the number of T sites per 1000 Å^3 in a zeolite must be less than 20. The *NodeType* line defines the number of bonds for a given node type, the maximum number of nodes of this type in the asymmetric unit, and a list of the symmetry elements that cannot be occupied by a node of this type. The *EvenLoopSizesOnly* option was introduced for the search for frameworks where a strict alternation of two atom types is expected. In these cases, only even loop sizes are possible. This is especially useful in the case of aluminophosphates, where the scattering powers of Al and P are very similar, so the atoms cannot be distinguished from one another easily. The *Check3-DimConnectivity* keyword is used to turn a filter procedure *On* or *Off*. If it is *On*, only three-dimensionally connected frameworks are accepted, and layer or chain structures are rejected.

The next input block describes the initialization and development of the 'trials'. Each new starting phase set generated prior to the Fourier recycling procedure (see Fig. 1) is considered to be a trial. The *FeedBackCycles* keyword is followed by an arbitrarily long sequence of integers which define the recycling steps. The first

integer specifies the number of times the atom recycling procedure is to be used in the first step of one trial, the second integer is for the number of framework-fragment recycling loops in the second step, the third again for atom recycling in the third step, and so on. Experience has shown that a simple alternation of these two modes, as indicated in Fig. 2, is usually the most efficient approach.

The next block concerns the layout of the electron density map and the characteristics of the peak search and refinement. The last block in Fig. 2 specifies the treatment and usage of the extracted intensities. The *OverlapFactor* together with the individual full width at half maximum (FWHM) for each reflection is used to determine the overlap groups. *ReflectionUsage* specifies the number of reflections that are actually used. This can be absolute, for example 'ReflectionUsage 80' will select the 80 highest reflections, or it can be relative, as in Fig. 2. In the latter case, reflections are selected in descending order of (equipartitioned) structure factor times multiplicity (MF) until the prescribed percentage of the total sum of MF over all input reflections is accumulated.

The last part of the input file, which is not shown in Fig. 2, is a listing of the extracted structure-factor magnitudes, $|F|$. The data are given as reflection indices *hkl*, observed relative $|F|$, the standard uncertainty of $|F|$ (if available) and the FWHM as derived from the refined profile parameters.

3.2. *Repartitioning of overlapping intensities with FIPS*

The *FIPS* method (Estermann & Gramlich, 1993) was used to repartition the overlapping intensities extracted from the SNBL powder pattern of YUL-86. In this case, FIPS can be expected to work well, because the ratio of overlapping to nonoverlapping reflections is sufficiently low (309 overlapping and 142 nonoverlapping reflections). The critical input parameters for FIPS are the α parameter (Estermann & Gramlich, 1993) and the number of FIPS cycles. The goal is to find the α and the corresponding number of FIPS cycles, which minimize the figure of merit Δ (Estermann & Gramlich, 1993). Therefore, α values between 2 and 20 were tried systematically in steps of 1. The best figure of merit was obtained with one *FIPS* cycle and $\alpha = 19$.

3.3. *Results of the FOCUS runs*

Two more *FOCUS* input files were derived from the one shown in Fig. 2. In the second input file, the intensities extracted from the Stoe measurement were replaced with the intensities extracted from the SNBL measurement. The third input file was based on the second one. In this case, the extracted intensities were replaced with the repartitioned intensities obtained from *FIPS*.

Each of the input files was used in turn for a *FOCUS* run with 1000 trials. The run time with each input was about 80 min on a Silicon Graphics R10000/180 MHz CPU. The *FOCUS* output was then used to prepare the three histograms given in Fig. 3. These show how often each of the unique framework topologies was found [further information can be found in the work of Grosse-Kunstleve *et al.* (1997)]. In all three cases, the most frequently occurring topology is identical to the $AlPO_4$-21 framework topology with three Al, three P and 12 O atoms in the asymmetric unit. However, the absolute success rate (number of times the $AlPO_4$-21 topology was found in 1000 trials) is only 11 for the Stoe measurement, but 36 for the SNBL measurement with equipartitioned intensities, and 49 with intensities repartitioned using *FIPS*. This result underlines the superior quality of the synchrotron data and also the usefulness of *FIPS*.

Since there are ten recycling steps per trial (see *FeedBackCycles* in Fig. 2), the correct topology is, in general, found repeatedly in a successful *FOCUS* trial. For example, the 49 correct topologies found with the SNBL/*FIPS* input were produced in 20 trials. This means that on average a correct topology was found once in every 50 trials, or once every 2 min.

4. Structure determination for the aluminophosphate YUL-90

The *FOCUS* input file for YUL-90 was generated using the considerations outlined above for YUL-86. The

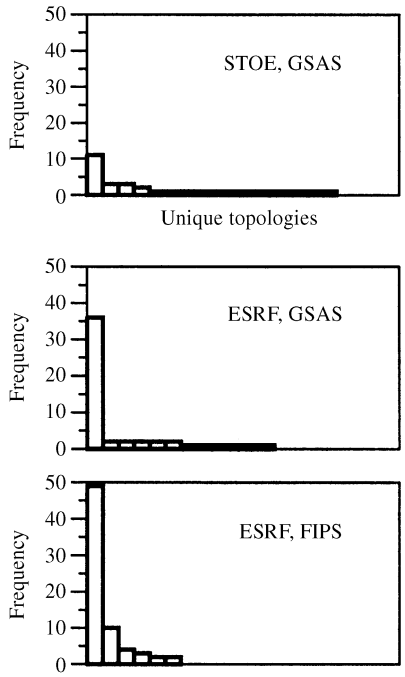

Fig. 3. *FOCUS* histograms for YUL-86; 1000 trials per run.

FIPS method was used to repartition the intensities extracted from the Stoe measurement, and the optimal value for α and the corresponding number of *FIPS* cycles were determined to be $\alpha = 4$ with six *FIPS* cycles.

2000 *FOCUS* trials were executed in about 13.5 h using a Silicon Graphics R10000/195 MHz processor. The result of this run is summarized in the histogram in Fig. 4. Only five unique framework topologies were found. The most frequently occurring topology (four Al, four P and 16 O atoms in the asymmetric unit) was found 21 times in 11 *FOCUS* trials and is identical to the ZON topology in the *Atlas of Zeolite Structure Types* (Meier *et al.*, 1996). This means that on average the correct topology was found once in every 182 trials, or once every 73 min.

5. Complex test case I: ZSM-5

For this test, data were collected on the as-synthesized material (*i.e.* with tetrapropylammonium ions in the pores). In this form, ZSM-5 is orthorhombic with a unit-cell volume of *ca* 6000 Å^3. The relevant data for the SNBL data collection and the full profile intensity extraction with *GSAS* are summarized in Table 1. All parameters in the *FOCUS* input file had default values based on the considerations outlined by Grosse-Kunstleve *et al.* (1997).

7000 *FOCUS* trials were executed in about 9.2 h using a Silicon Graphics R10000/195 MHz processor. As is shown in Fig. 5, only three unique topologies were found. The correct MFI topology of ZSM-5 occurred 81 times in 29 trials. This means that on average the correct topology with 12 Si and 26 O atoms in the asymmetric unit was found once in every 241 trials, or once every 19 min.

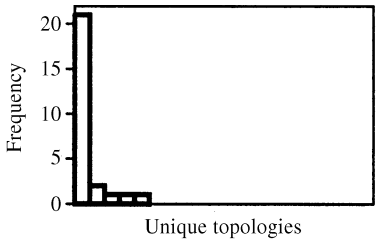

Fig. 4. *FOCUS* histogram for YUL-90; 2000 trials.

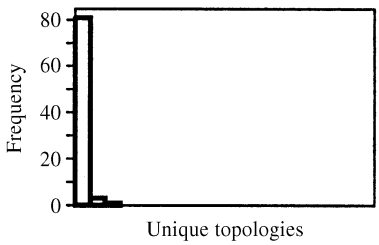

Fig. 5. *FOCUS* histogram for ZSM-5; 7000 trials.

6. Complex test case II: cloverite

As a preliminary test, synthetic single-crystal data were computed from the refined cloverite structure in the space group $Fm\bar{3}c$ ($a \simeq 51.6$ Å), and a *FOCUS* input file was prepared. With this input, the correct framework with ten T sites (five Ga and five P) could be found 91 times in 38 of 662 trials. For the next test, peak half widths (FWHM) typical for synchrotron experiments were assigned to the calculated intensities, and the overlapping intensities equipartitioned. The overlap factor used was 0.15 (corresponding to 30% FWHM), which is a conservative estimate. However, with this input, the correct topology could not be found at all in the space group $Fm\bar{3}c$. Obviously, tackling this combination of a complex structure and an extremely high percentage of overlapping reflections (92% at a resolution of 1.4 Å) is beyond the capabilities of *FOCUS*. In an attempt to improve the equipartitioned intensities, the *FIPS* method was tried, but the ratio of overlapping to nonoverlapping reflections is too high for *FIPS* to improve the partitioning. In summary, with the methods available it seems very unlikely that the cloverite structure could be solved from powder data in the space group $Fm\bar{3}c$.

However, most of the peaks in the powder pattern of cloverite can be indexed using a primitive cubic unit cell with $a \simeq 25.8$ Å. Only a series of weak superlattice reflections require the doubling of the lattice parameter. Even for the initial structure solution from single-crystal data (Estermann *et al.*, 1991), it was assumed that the Ga–P ordering could be ignored, and the small unit cell and the space group $Pm\bar{3}m$ used. Therefore it seemed fair to apply the same assumption to the structure solution from powder data.

For the tests with *FOCUS*, the synchrotron powder data collected by Estermann *et al.* (1991) were used. Integrated intensities were extracted with *GSAS* and processed as described before. The relevant data are summarized in Table 1. Because of the high degree of overlap, the *FIPS* method was not applied.

The *FOCUS* input file on which the following results are based is the result of a sequence of attempts to find the 'right' parameters. There are significant deviations from the default choices for several parameters. Vanadium was used as an approximation to an averaged Ga/P pseudo-atom. As an experiment, oxygen was used in the atom recycling procedure, but only a maximum of 192 atoms (number of framework nodes) were actually recycled. *MaxSymNodes* was set based on the 'maximum of 20 T sites per 1000 Å^3' assumption introduced before. All these choices are still quite obvious. However, the introduction of a second *NodeType* definition for the three-connected nodes of course requires the knowledge

or at least the suspicion that the solution is an interrupted framework.

Allowing for the three-connected node type has two unpleasant consequences. The time spent for the framework searches increases significantly, and a huge number of very low-density interrupted frameworks are produced. If the default value of 0 is used for *MinSymNodes*, the correct framework is usually hidden in the tails of the *FOCUS* histograms. Therefore it is necessary to use *MinSymNodes* to set a lower boundary for frameworks considered feasible. In the present case, a minimum of ten framework nodes per 1000 Å^3 was assumed, which corresponds to 172 nodes per unit cell. (The assumption would be valid for all zeolite frameworks known.)

13 000 FOCUS trials were executed in about 77 h using a Silicon Graphics R10000/195 MHz processor. As can be seen in the resulting histogram shown in Fig. 6, 19 unique topologies were found. The correct -CLO topology (*Atlas of Zeolite Structure Types*) of cloverite, with five Ga/P and 14 O atoms in the asymmetric unit, is represented by the first bar in the histogram and occurred 23 times in nine trials. This means that on average the correct topology was found once in every 1444 trials, or once every 8.6 h.

7. Discussion

For zeolites, *FOCUS* can be more successful than other methods, because more prior knowledge is integrated into the solution process. However, in the case of cloverite, is was not known beforehand that the framework was interrupted [though infrared spectra would have made this apparent (Barr *et al.*, 1993)]. Not knowing the solution also implies that there is no certainty that the unit cell is correct and generally that several space groups are feasible. For example, from the apparent systematic absences, there are five choices for the space group of cloverite (in the smaller primitive cubic cell). Given the large fraction of overlapping intensities and the large unit cell, significant effort would be required to try all space groups, even assuming that the framework is fully four-connected. The fact that the framework is interrupted complicates the matter further. The correct solution (and space group) would be one of several possibilities and could only be selected on the basis of the outcome of a Rietveld refinement. Nonetheless, given enough computer time and some 'thinking', this structure could have been solved eventually using this method. For such borderline cases where computing time becomes a limitation, the generation of a structure envelope (Brenner *et al.*, 1997) to restrict the regions of the asymmetric unit in which the structure is to be sought might accelerate structure solution.

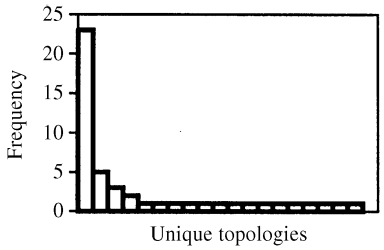

Fig. 6. *FOCUS* histogram for cloverite; 13 000 trials.

On the other hand, the only difficulty with the ZSM-5 test case was the careful adjustment of the *MaxPeaksFwSearch* and *MaxPeaksFwFragmentSearch* parameters to keep the computing time required reasonable. The choices for all the other input parameters have default values which were derived from other extensive tests described in detail by Grosse-Kunstleve (1996). Since ZSM-5 is a high-silica zeolite with all framework nodes four-connected, it is an ideal structure for the application of *FOCUS* even though it is complex. The solution can be expected to become apparent in the histogram in just a few hours.

The fact that the YUL-86 and YUL-90 structures were solved without our knowing the framework topology beforehand, essentially with default input parameters for aluminophosphate materials, shows that *FOCUS* is capable of solving average zeolite structures in very little time, compared to the time needed for other steps shown in Fig. 1. For example, the unit-cell and space-group determination for YUL-90 took several days and often required manual intervention, but the correct topology can be expected to appear as the largest bar in the *FOCUS* histogram after only a few hours of a fully automatic search. Since the histograms can be generated while *FOCUS* is still running, the search can be monitored and terminated as soon as the statistics of the histogram are sufficiently clear.

The framework topologies of the structures presented in this paper were (or turned out to be) already known. Therefore it was not necessary to conduct Rietveld refinements in order to confirm the solutions obtained with *FOCUS*. However, for structures with novel topologies, Rietveld refinement is an essential step to confirm the solution. For average zeolites, this step typically takes an order of magnitude longer then the actual determination of the framework topology. To remove this bottleneck, more powerful structure completion and refinement methods would be highly desirable.

We thank Professors J.-L. Guth and H. Kessler for providing us with the aluminophosphate and cloverite samples. We also thank the SRS in Daresbury and the SNBL at the ESRF in Grenoble for allowing us access to their synchrotron radiation facilities. This work was supported in part by the Swiss National Science Foundation.

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